

- Lyman, W.J., Reehl, W.F. and Rosenblatt, W.F., 1982. Handbook of Chemical Property Estimation Methods—Environmental Behaviour of Organic Compounds. McGraw-Hill, New York, N.Y., 1000 pp.
- Mikesell, M.D. and Boyd, S.A., 1988. Enhancement of pentachlorophenol degradation in soil through induced anaerobiosis and bioaugmentation with anaerobic sewage sludge. *Environ. Sci. Technol.*, 22: 1411–1414.
- Schellenberg, K., Leuenberger, C. and Schwarzenbach, R.P., 1984. Sorption of chlorinated phenols by natural sediments and aquifer materials. *Environ. Sci. Technol.*, 18: 652–657.
- Schultz, B., 1983. Determination of priority pollutant nitrophenols in water by high-performance liquid chromatography. *J. Chromatogr.*, 269: 208–212.
- Sufita, J.M., Horowitz, A., Shelton, D.R. and Tiedje, J.M., 1982. Dehalogenation: A novel pathway for the anaerobic biodegradation of haloaromatic compounds. *Science*, 218: 115–117.
- Ulrich, H.-J. and Stone, A.T., 1989. Oxidation of chlorophenol adsorbed to manganese oxide surfaces. *Environ. Sci. Technol.*, 23: 421–428.
- Westall, J.C., Leuenberger, C. and Schwarzenbach, R.P., 1985. Influence of pH and ionic strength on the aqueous-nonaqueous distribution of chlorinated phenols. *Environ. Sci. Technol.*, 19: 193–198.
- Woods, S.L., Ferguson, J.F. and Benjamin, M.M., 1989. Characterization of chlorophenol and chloromethoxybenzene biodegradation during anaerobic treatment. *Environ. Sci. Technol.*, 23: 62–68.
- Worthing, C.R., 1979. The Pesticide Manual. Br. Crop Prot. Council, London, 6th ed., 655 pp.



Best Available Copy

THE SEPARATION OF RADIONUCLIDE MIGRATION BY SOLUTION AND PARTICLE TRANSPORT IN SOIL

J. TOROK, L.P. BUCKLEY and B.L. WOODS

Waste Management Technology Division, Chalk River Nuclear Laboratories, Chalk River, Ont. K0J 1J0 (Canada)

(Received May 22, 1989; revised and accepted April 11, 1990)

ABSTRACT

Torok, J., Buckley, L.P. and Woods, B.L., 1990. The separation of radionuclide migration by solution and particle transport in soil. *J. Contam. Hydrol.*, 6: 185–203.

Laboratory-scale lysimeter experiments were performed with simulated waste forms placed in candidate buffer materials which have been chosen for a low-level radioactive waste repository. Radionuclide releases into the effluent water and capture by the buffer material were determined. The results could not be explained by traditional solution transport mechanisms, and particle transport was suspected as the dominant mechanism for radionuclide release from the lysimeters. To elucidate the relative contribution of particle and solution transport, lysimeter wastes were replaced by a wafer of neutron-activated buffer soaked with selected soluble isotopes. Particle transport was determined by the movement of gamma-emitting neutron-activation products through the lysimeter. Particle capture filtration and adsorption coefficients were calculated. Solution transport was quantified by comparing the migration of soluble radionuclides relative to the transport of neutron-activation products. Distribution coefficients and rate constants of radionuclide desorption were calculated directly from buffer cores, and rate constants for radionuclide adsorption were then approximated. The results of this experiment and modelling of the solution transport process were used to determine the radionuclide transport mechanism in experiments with simulated waste forms in the lysimeters. The mechanisms are as follows: ^{137}Cs release is attributed to the adsorption of soluble ^{137}Cs onto colloid clay particles followed by clay particle transport; ^{60}Co was incorporated as particles within the waste form and released as colloids. The new approach presented here for monitoring radionuclide migration in soil facilitates the determination of most of the fundamental coefficients required to model the transport process.

INTRODUCTION

There are several potential mechanisms for the aqueous transport of radionuclides in porous media. The most important mechanisms include solution transport of ionized and complexed species, and particle transport of colloids and pseudocolloids. To elucidate the dominant transport mechanism and hence predict the long-term behaviour of radionuclides in natural or man-made porous media, the accepted methodology is to match the experimental results with its mathematical simulation. A close match is presumed to be a confirmation of the transport mechanism implicit in the simulation. The simulation

ADMIN RECORD

SW-A-004581

DOCUMENT CLASSIFICATION
REVIEW WAIVER PER
CLASSIFICATION OFFICE

of particle transport is especially difficult because of the large number of parameters that have a major effect on the transport, such as surface charge, particle size distribution, the degree of consolidation of the media and channeling in the media. The rather crude match between the experiments and their simulation in natural systems is often attributed to the extreme spatial variability of soil properties.

An approach is outlined where the contribution of particle transport and solution transport of strongly adsorbing cations can readily be resolved and quantified, irrespective of the structural inhomogeneities present in the porous media. Basically the experiments involve the introduction of dissolved radioactive species in combination with their adsorbent into the porous media with saturated or unsaturated flow passing through the media. A portion of the adsorbent is neutron activated, equilibrated with the soluble radionuclide and then introduced into the porous medium. Particle transport is determined by the migration of neutron-activation products, while solution transport is computed from the difference between the migration of dissolved radionuclides and neutron-activation products. In the experiment outlined in this paper, the migration of soluble ^{60}Co , ^{85}Sr and ^{137}Cs and neutron-activated clay were monitored simultaneously. Champlin and Eichholz (1976) performed experiments very similar to the ones reported here. They introduced neutron-activated kaolin, a soluble salt of ^{86}Rb , and ^{140}La -labeled bacteria into a soil column. However, they did not observe transport of radionuclides by the neutron-activated kaolin pseudocolloids because ^{86}Rb migrated exclusively by solution transport mechanism due to its low distribution coefficient, and thus the contribution of the solution and particle transport mechanisms for this isotope did not need to be isolated.

The experimental approach outlined above was used in the analysis of combined radionuclide leaching and migration studies in laboratory-scale lysimeter experiments. There are several advantages to the performance of lysimeter experiments as opposed to a mathematical combination of the results of leaching and transport experiments usually done in repository modelling. Radionuclides are not necessarily released from the waste forms as dissolved ionized species as generally assumed for the source term in transport experiments, but may also be incorporated into insoluble particles and/or organic complexes. Lysimeters also realistically simulate the inhomogeneities of repositories and the physical and chemical environment present in the repositories.

LABORATORY-SCALE LYSIMETER EXPERIMENTS

The development of the approach outlined in the Introduction was prompted by difficulties in the interpretation of laboratory-scale lysimeter results (Buckley et al., 1987). The lysimeters formed part of a program to qualify an engineered barrier, i.e. a buffer layer placed at the bottom of a low-level radioactive waste repository, designed to effectively retard the migration of

radionuclides and also facilitate the drainage of water. Because of this latter requirement, the structure of the buffer cannot be as compact as low-permeability natural clay formations. The more porous structure of the buffer will allow transport of particles during infiltration or flooding.

The lysimeter experiments were performed to couple the leaching of waste forms with the migration of radionuclides through buffer materials. The experimental program and some of the results have been reported before (Buckley et al., 1987, 1988; Torok and Buckley, 1988). The waste forms, placed in the centre of the lysimeters, were sodium phosphate traced with ^{60}Co , ^{85}Sr and ^{137}Cs , and immobilized in bitumen. The buffer material surrounding the waste was a 90:10 weight ratio of local coarse (0.2 mm) fluvial sand and clay obtained from the Dochart Brick and Tile Company Limited in Aronprior, Ontario. It is a local glacial deposit containing rock flour, illite and chlorite. About a 5-6-cm-thick buffer layer separated the waste form from the drain. A schematic diagram of the lysimeter is shown in Fig. 1. The lysimeters were subjected to infiltration for up to 115 days. Radionuclide content of the effluent water and of the buffer cores upon completion of the infiltration was determined. The early breakthrough of all three isotopes was inconsistent with a solution

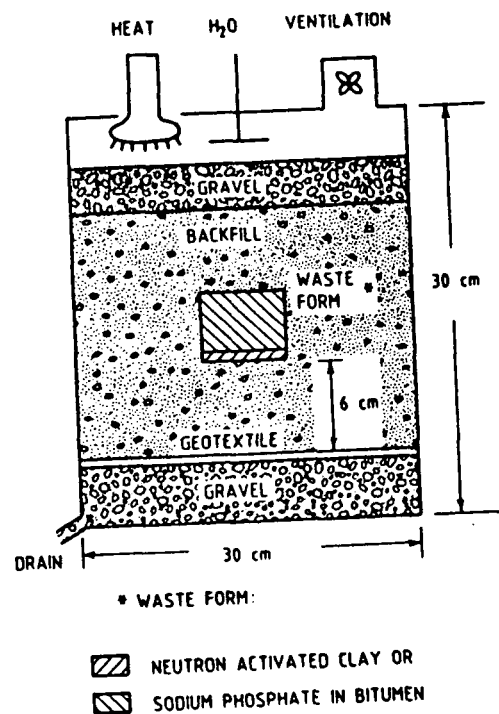


Fig. 1. Schematic of the lysimeter.

transport mechanism considering the relatively high distribution coefficients obtained in batch-type experiments for all three isotopes. The observed phenomenon is more consistent with particle transport.

To elucidate the transport mechanism, a few grams of clay were neutron activated, thoroughly mixed with a larger portion of sand-clay buffer, and then soaked with a solution of ^{60}Co , ^{85}Sr and ^{137}Cs . A 1-cm-thick layer of this source material was incorporated into a lysimeter where the bottom of the waste form was located in previous lysimeter experiments (see Fig. 1). Experiments indicated that all of the gamma-emitting neutron-activation products were associated with the clay portion of the buffer and were not desorbed from it when equilibrated with water. Thus, any displacement of activation products would be exclusively due to particle transport. The radionuclide content of the effluent water was monitored during each of the two lysimeter experiments. At the end of each experiment, the buffer was cored at the centre and the radionuclide content of thin buffer slices was determined. To evaluate the spreading of neutron-activated clay during lysimeter packing and coring, an identical control lysimeter was prepared without the dissolved radionuclide addition. The control lysimeter was not subjected to water infiltration, but was cored soon after packing.

RESULTS

Results from lysimeters containing neutron-activated clay are presented first. The results are then applied in the interpretation of data obtained from lysimeters containing bituminized waste forms.

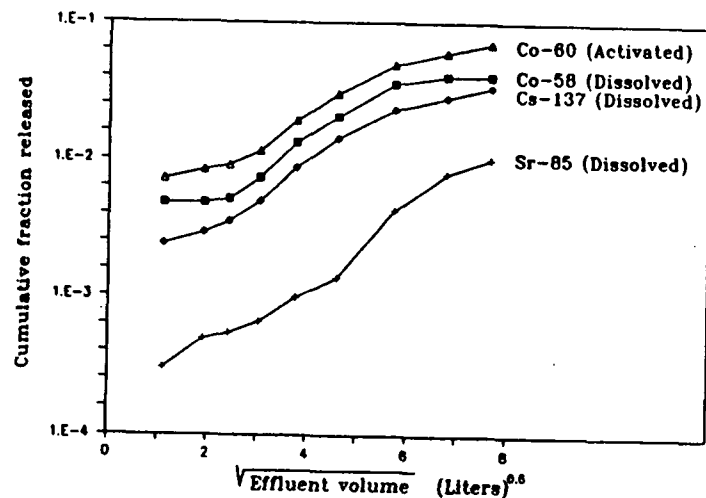


Fig. 2. Radionuclide release from lysimeter containing activated clay and dissolved radionuclides.

Lysimeters containing neutron-activated clay

Only results from one of the two lysimeter experiments are reported for brevity. The results from the two experiments were very similar. Gamma spectrometry of the effluent water from the lysimeter containing activated buffer and dissolved radionuclides is illustrated in Fig. 2. The data are presented as the cumulative fraction of inventory eluted as a function of square root of the effluent volume. Clay particle transport can be estimated from ^{60}Co , a dominant gamma-emitting activation product. Dissolved radionuclides added to the activated buffer and released from the lysimeter are included in Fig. 2. The elution pattern of ^{85}Sr is very similar to the elution pattern of the other activated and dissolved radionuclides albeit at $\sim 10\%$ of their relative concentrations. The concentrations of the radionuclides from a vertical buffer core taken at the end of the experiment are presented in Fig. 3. The elution pattern for ^{60}Co , a tracer for the clay particles, and the pattern for ^{58}Co and ^{137}Cs in both the effluent water and in the buffer cores are very similar and suggest that the latter two radionuclides were strongly bound to clay particles and were eluted with them with only limited desorption taking place during transport.

Solution transport. In Fig. 3, solution transport causes the ^{137}Cs peak to shift $\sim 1.5\text{ mm}$ downstream from the ^{60}Co peak. From this shift and the total linear displacement of water during infiltration, the retardation factor of 375, corresponding to a distribution coefficient (K_d) of 79, was calculated. The ^{58}Co data points were too few to facilitate a detailed analysis of peak shape, though it appears to be identical to the particle transport rate because the available data points nearly coincide with one of the activation products: ^{60}Co . The ^{85}Sr peak migrated downstream 14 mm and also broadened, consistent with a liquid-

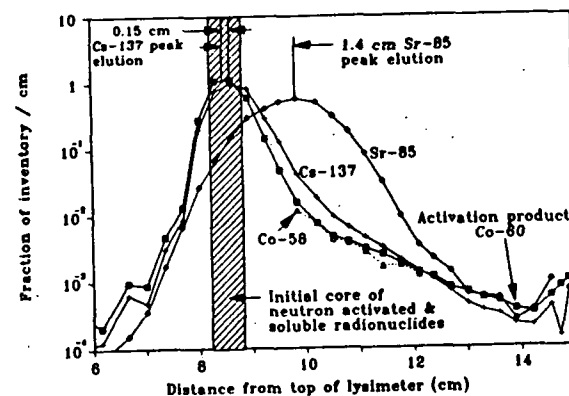


Fig. 3. Radionuclide concentration in lysimeter core containing activated clay and dissolved radionuclides.

phase transport mechanism. For ^{85}Sr , the retardation factor is 40 ($K_d = 8$) based on peak displacement.

Particle transport. The transport of neutron-activated clay particles by infiltrating flow was estimated from the difference between the concentration of those particles in the lysimeters used for infiltration and the control lysimeter. This procedure compensated for the mixing of radionuclides during packing and coring. The concentration profiles of three activation products in the control lysimeter are presented in Fig. 4. The ^{60}Co peaks in the control and infiltration lysimeter cores were shifted to obtain coincidence of the peaks. The results are presented in Fig. 5. The difference in concentration (dC) downstream of the peak was computed. The semi-logarithmic plot of dC as a function of distance is presented in Fig. 6. The data can be fitted with two straight lines. Very similar results were obtained by Eichholz et al. (1982) when neutron-activated clay particles were added to water that percolated through a column close to the source and particle adsorption further downstream. Saltelli et al. (1984) developed a mathematical model for colloid filtration that accounts for both of the above particle capture mechanisms. Capture coefficients (w) were calculated for the filtration and particle adsorption processes for mono-dispersed particles using the following relationship:

$$C = C_0 \exp(-wX) \quad (1)$$

where C is the concentration of neutron-activation product (that is proportio-

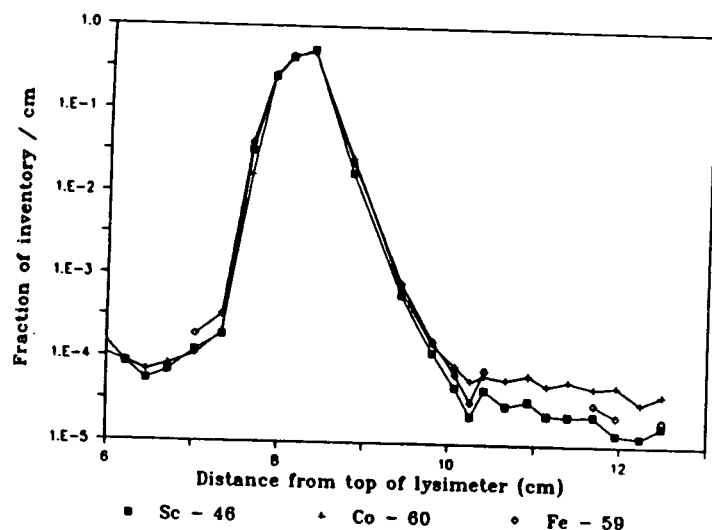


Fig. 4. Neutron-activation products in the core of the control lysimeter.

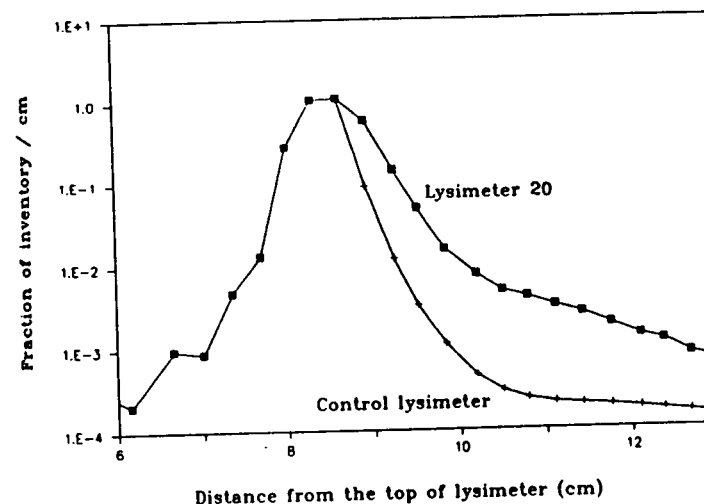


Fig. 5. Neutron-activation product (^{60}Co) in the core of the percolating and control lysimeters.

nal to particle concentration) at a distance, X , into the bed; and C_0 is the initial concentration. The values of w for filtration and particle adsorption were 0.3 and 0.083 mm^{-1} , respectively. Natural colloids, such as clay particles responsible for radionuclide transport in this system, usually have log-normal particle-size distribution (Travis and Nuttal, 1985). It is thus surprising and as yet unexplained in these experiments that the particle transport conforms to dynamics that are characteristic of the filtration of mono-dispersed particles.

Desorption of ^{137}Cs from mobile particles. Due to water infiltration, there is a net migration of dissolved radionuclides and suspended colloid particles. The radionuclide peak migrates at a velocity equal to water velocity divided by the retardation factor. The colloid particles migrate at a velocity that is very near or equal to the water velocity. The particle moves ahead of the radionuclide peak, and enters a region where the radionuclide concentration in solution is orders of magnitude lower than in its previous environment. The rate of radionuclide adsorption becomes negligible and the particle loses its radionuclide content at a rate equal to the desorption rate. Assuming that desorption follows first-order kinetics:

$$dC^*/dt = -GC^* \quad (2)$$

where C^* = adsorbed radionuclide concentration; G = first-order desorption rate constant; and t = time.

In the region of the lysimeter where particle transport of radionuclides

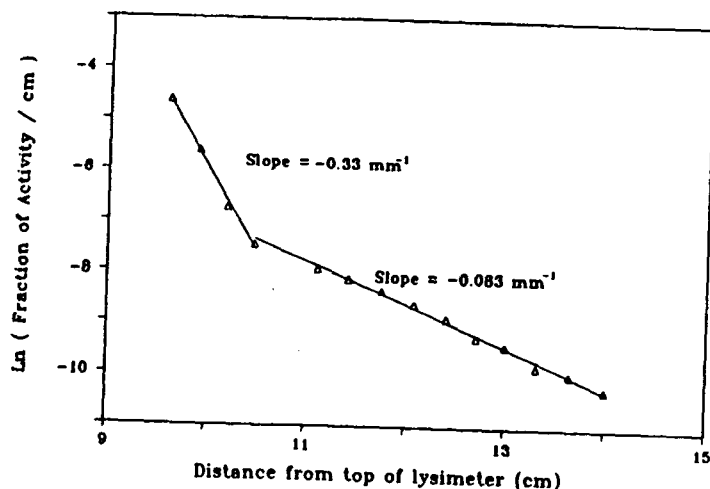


Fig. 6. Neutron-activation products in percolating lysimeter corrected for mixing (from control lysimeter).

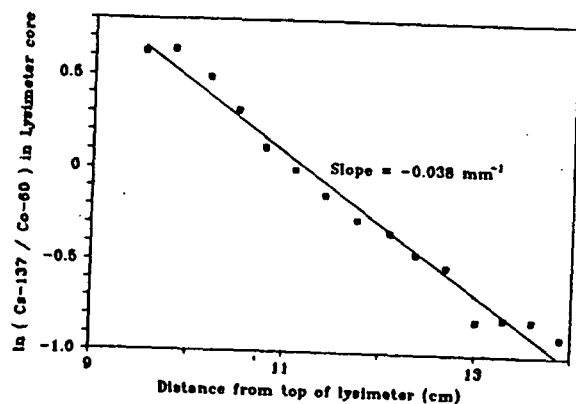


Fig. 7. Desorption of ^{137}Cs from colloid particles.

dominates, the decline in radionuclide concentration with distance from the source can be expressed by the following relationship:

$$\ln (C^*/C) = \ln (C_0^*/C_0) - (G/V)X \quad (3)$$

where C_0^* = initial adsorbed radionuclide concentration; and V = pore-water velocity.

For the derivation of eq. 3, see the Appendix.

A semi-logarithmic plot of the ratio of $[^{137}\text{Cs}]/[^{60}\text{Co}]$ as a function of distance in the lysimeter is presented in Fig. 7. The slope of the line is equal to $-G/V$ from eq. 3. The pore-water velocity in the lysimeter was 2.67 mm h^{-1} . The desorption rate constant is thus $2.8 \cdot 10^{-5} \text{ s}^{-1}$, corresponding to a desorption half-life of 6.3 h. A similar calculation for ^{85}Sr was not possible from this experiment because the peak has migrated too far downstream in the buffer medium and thus it masks most of the activity deposited by particle transport.

Calculation of the adsorption rate constant

As indicated before, at equilibrium the adsorption and desorption rates are equal. If we assume adsorption is a first-order process than from the desorption rate constant calculated on p. 191 and the distribution coefficients (K_d) calculated from peak shifts, the adsorption rate constant, A , can be calculated:

$$A = GK_d \quad (4)$$

The calculated adsorption rate constant for ^{137}Cs is $8.3 \cdot 10^{-5} \text{ s}^{-1}$ corresponding to an adsorption half-life of 1.4 min. The value of the adsorption rate constant is only approximate because the distribution coefficient was obtained for the buffer material and the forward rate constant for the colloid clay particles responsible for particulate transport. Thus the validity of the estimate for adsorption coefficient is dependent on the close correspondence between the above two distribution coefficients. Sheppard et al. (1980) found that Cs is attached to clay particles in proportion to the particle volume and thus the mobile colloid particles at the smaller end of the soil particle size distribution may have similar distribution coefficient as the bulk stationary particles.

MECHANISM OF RADIONUCLIDE TRANSPORT WITH BITUMINIZED SODIUM PHOSPHATE WASTE FORMS

Data from lysimeters containing two candidate buffer materials, sand-clay and sand-clinoptilolite mixtures, were analyzed to explore differences in the transport mechanism. Lysimeter operating conditions are listed in Table 1.

Experiments with sand-clay buffer

To compare the lysimeter experiments with activated clay and with bituminized sodium phosphate waste forms, the following calculations were performed:

(a) The laboratory leach results of bituminized sodium phosphate waste form (BW) with deionized water as leachant were used as source term for ^{137}Cs and ^{60}Co . They are plotted in Figs. 8 and 9, respectively.

(b) Soluble radionuclide release data from the lysimeter containing neutron-activated clay (NAC) were combined into a mathematical model of the lysimeter.

TABLE 1

Lysimeter operating conditions

Hydrodynamics	pore-water velocity	2.7 mm h ⁻¹
	water infiltration rate	0.96 kg m ⁻² h ⁻¹
	degree of saturation	~100%
Lysimeter cross-sectional area		0.073 m ²
Waste form	composition	40 wt.% trisodium phosphate in bitumin containing ¹³⁷ Cs, ⁶⁰ Sr and ⁶⁰ Co
	size in lysimeter experiments	4.7 cm diameter, 5 cm high
	size in leaching experiments	2.5 cm diameter, 6 cm high
Buffer	90:10 sand-clay	
	bulk density	1.72 Mg m ⁻³
	porosity	0.361 m ³ m ⁻³

The following approach was used in the simulation of particle transport in the lysimeter containing bituminized waste. The results of activity released in laboratory leaching tests of BW was arbitrarily divided into twelve equal time periods. The radio-activity leached in each time period was then used as a source term in the next stage of the calculation, where activity release from the lysimeter was computed from the experiments with NAC. Computed release from each time period was then summed to obtain the total release. The above approach to the calculation is illustrated in Fig. 10.

For the lysimeter containing the neutron-activated clay, all of the soluble radionuclides are adsorbed by the buffer at the beginning of the experiment; for the lysimeter containing bituminized sodium phosphate, the radionuclides are released gradually. The assumptions in the above model are that the radionuclides leave the bituminized waste form as dissolved species and are chemisorbed on the surface of the buffer components adjacent to the waste form. The radionuclides then move through the buffer layer primarily by particle transport. Results of these calculations, the waste form leaching results, and the actual radionuclide release from the lysimeters are presented in Figs. 8 and 9 for ¹³⁷Cs and ⁶⁰Co, respectively.

Cesium transport mechanism

In Fig. 8, a comparison of the waste-form ¹³⁷Cs leach rate and release rate from the lysimeter indicates a significant retardation of ¹³⁷Cs in the buffer layer with the amount released about three orders of magnitude lower than the amount leached. Calculated and actual release from the lysimeter differ by about a factor of 2-8, a relatively small difference compared to the capture of ¹³⁷Cs by the buffer layer. Thus, the leaching and transport mechanism assumed in the model outlined above is plausible for ¹³⁷Cs.

THE SEPARATION OF RADIONUCLIDE MIGRATION

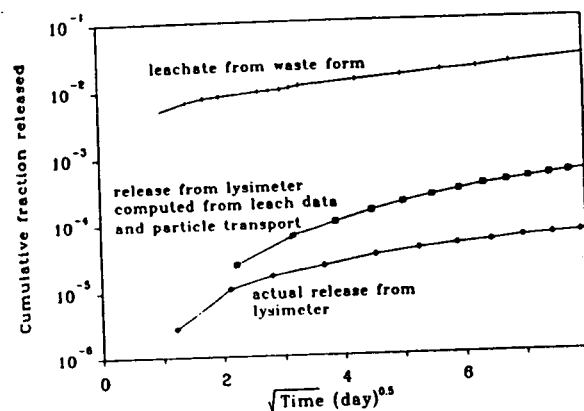


Fig. 8. ¹³⁷Cs released from lysimeter and leached from waste form (buffer in lysimeter: 90:10 sand-clay; waste form: 40 wt.% trisodium phosphate in bitumen).

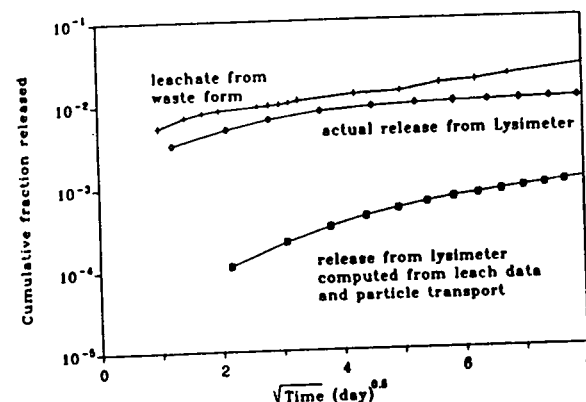


Fig. 9. ⁶⁰Co released from lysimeter and leached from waste form (buffer in lysimeter: 90:10 sand-clay; waste form: 40 wt.% trisodium phosphate in bitumen).

Cobalt transport mechanism

Comparison of Figs. 8 and 9 indicates a different behaviour of ⁶⁰Co from that of ¹³⁷Cs. A significant portion of ⁶⁰Co leached from the waste form was released from the lysimeter. Soluble cobalt salts soaked into buffer were retarded much more effectively than ⁶⁰Co leached from the waste. Explanations for the low retention of ⁶⁰Co described above include: (1) the release of colloid, rather than

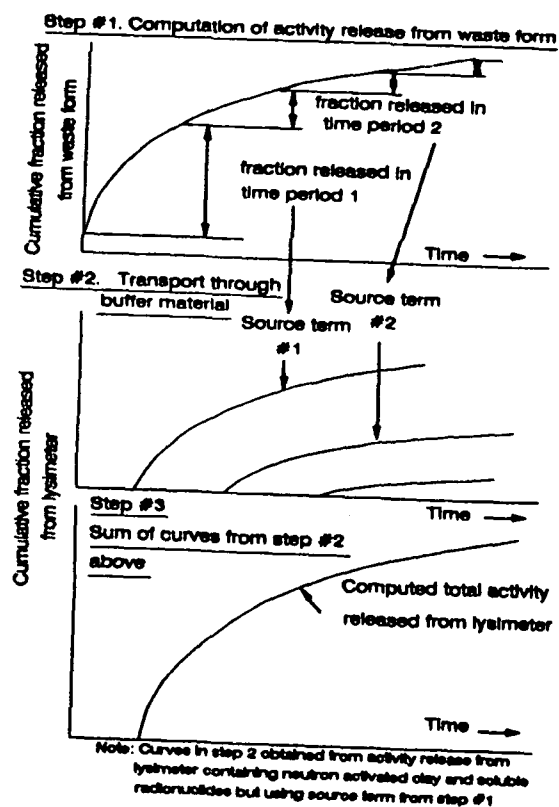


Fig. 10. Schematic diagram of simulation calculations.

dissolved Co species from the waste form; and (2) a significant lowering of its distribution coefficient due to the presence of phosphate ions. In the next section, we examine the validity of each of the above two potential explanations to identify the most plausible one.

Release of colloid cobalt species from the waste form. The simulated bituminized waste was prepared by the dissolution of trisodium phosphate and the introduction of radionuclide solution followed by drying of the solution and incorporation of the solid into the bitumen. The sodium phosphate solution is basic. As an example, a 0.1 N trisodium phosphate solution has a pH of 12. The Co^{2+} salt introduced into the waste form is unstable at this high pH. It readily forms cationic aggregates, i.e. highly charged inorganic polymer products (Gimblett, 1963; Nilsson et al., 1985). The $\text{Co}(\text{OH})_2$ colloid is positively charged (Parks,

1965) and since clay has a negative charge, the cobalt colloid would be expected to be absorbed by the buffer upon release. Based on the observed high mobility of the ^{60}Co in the lysimeters, it is more likely that the ^{60}Co was incorporated into the crystal structure of other, negatively charged colloids in the waste form. If the ^{60}Co in the waste form is associated with small colloid particles, then following release from the waste form, a large portion of these particles pass through the buffer without capture. This contrasts ^{137}Cs migration, where the radionuclide is released from the waste form as dissolved species and only a portion is captured by the clay colloids, and most of it fixed on immobile soil.

We have carefully examined the possibility of solution transport being responsible for ^{60}Co release because it is the only plausible alternative to colloid transport. Batch distribution coefficient experiments indicate that the ^{60}Co distribution coefficient is lowered by phosphate ions by over an order of magnitude to ~ 60 (Buckley et al., 1987). We also computed distribution coefficients from the radionuclide content of the liquid effluent released from the lysimeter at the end of the experiment and the radionuclide content of the bottom buffer core. For ^{60}Co , the geometric means distribution coefficient is 28 for 10 lysimeters containing bituminized or compacted waste forms. To differentiate between the two potential ^{60}Co transport mechanisms, the solution transport of ^{60}Co in the lysimeter was simulated using a one-dimensional solution transport model. This model predicted the breakthrough of ^{60}Co much later than observed, and soil ^{60}Co contents two to three orders of magnitude higher than observed. Thus, the magnitude and shape of the experimental curves are inconsistent with the solution transport mechanism.

Strontium transport mechanism

Due to water infiltration, there is a net migration of dissolved radionuclides and suspended colloid particles. The radionuclide peak migrates at a velocity equal to water velocity divided by the retardation coefficient. The colloid particles migrate at a velocity that is very near or equal to the water velocity. The particle moves ahead of the radionuclide peak, and enters a region where the radionuclide concentration in solution is orders of magnitude lower than in its previous environment. The rate of radionuclide adsorption becomes negligible and the particle loses its radionuclide content at a rate equal to the desorption rate. Since the desorption rate of radionuclides is expected to be low for radionuclides with high distribution coefficients, and high for radionuclides with low distribution coefficients, the radionuclide concentration in the initial breakthrough by particle transport is expected to be in the reverse sequence when compared to breakthrough by solution transport.

While the relative fraction of radionuclides released from the activated clay lysimeter was in the order: $^{60}\text{Co} > ^{137}\text{Cs} > ^{85}\text{Sr}$, the order in nearly all of the bituminized sodium phosphate lysimeters was: $^{60}\text{Co} > ^{85}\text{Sr} > ^{137}\text{Cs}$. In Table 2, the average distribution coefficients for batch and lysimeter experiments are summarized. It is apparent that the addition of phosphate reduces the ^{137}Cs

TABLE 2

Summary of distribution coefficients from batch determinations and lysimeter containing neutron-activated clay

Source	Water chemistry	Distribution coefficient (kg^{-1})		
		^{60}Co	^{137}Cs	^{85}Sr
Batch experiments (Buckley et al., 1987)	local groundwater	900	7,300	14
	demineralized water with phosphate	64	520	$> 10^6$
Lysimeter containing neutron-activated clay (Torok et al., 1988)	local groundwater	n.a.	79	8

n.a. = not available.

distribution coefficient and substantially increases the ^{85}Sr distribution coefficient. If we assume that both isotopes are transported by mobile clay colloids, then based on the principles outlined above, the change in relative concentrations can be attributed to the changes in distribution coefficients. However, it is difficult to explain how the sparingly soluble strontium phosphate is immobilized on colloid clay particles. Thus, further experiments are required to understand ^{85}Sr transport in the presence of phosphate ions in the sand-clay mix.

Experiments with sand-clinoptilolite buffer

Two of the lysimeters contained bituminized sodium phosphate waste form and the buffer was 90 wt.% sand-10 wt.% clinoptilolite. The clinoptilolite particles were the same size range as the sand, but contained some bentonite clay that readily washed out of its structure. Radionuclide concentration in the buffer below the waste form is presented in Fig. 11. According to filtration theory, the capture of monodispersed colloids in a packed bed would result in a linear relationship in Fig. 11 (Saltelli et al., 1984), the filtration of polydispersed particles results in a concave curvilinear relationship. The nearly linear curve for ^{60}Co suggests that the cobalt colloid is approximately monodispersed. In this experiment, ^{137}Cs and ^{85}Sr isotopes had identical concentration profiles and thus they were likely transported by an identical mechanism, most probably by polydispersed bentonite clay particles suggested by the concave curve in Fig. 11. Ohtsuka et al. (1988) found very similar radionuclide concentration profiles in a saturated sand aquifer for ^{137}Cs and ^{60}Co . They also attributed their finding to particle transport.

The effect of transients on radionuclide release

The hydrodynamic properties of freshly packed buffer are quite different

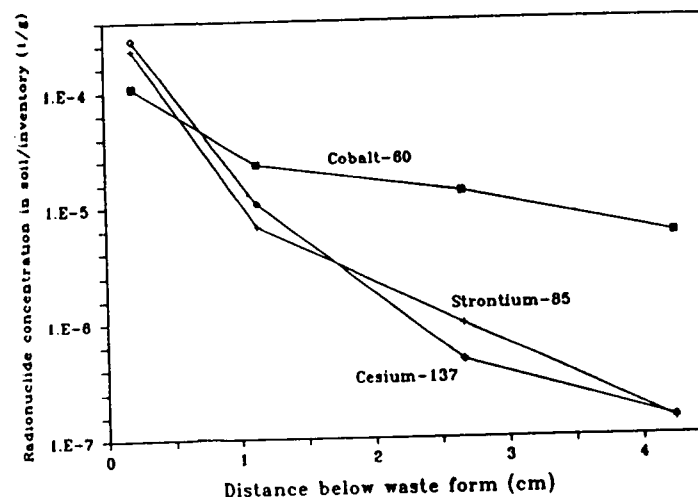


Fig. 11. Activity in buffer below waste form (waste for: phosphate in bitumen; buffer: sand-clinoptilolite).

from established buffers that have been subjected to several wetting and drying cycles. During infiltration into freshly packed buffer, structural changes take place in the buffer. In lysimeter experiments, it is difficult to precondition the buffer before the introduction of the waste form because the waste form introduction invariably disturbs the buffer structure. An example of the influence of transient conditions in lysimeter experiments is the release pattern of activated clay particles from the lysimeters. The particle concentration in the effluent water is equal to the difference between the rate of suspension of colloid particles and the rate of particle capture by the packed bed. In an established buffer, the suspension of particles is expected to be at steady state and reasonably constant. According to filtration theory, the particle capture is expected to decline with time as the bed becomes saturated. The expected net effect is an increase in release with time. Contrary to expectations, a general decline in particle release with time was experienced in three of the four lysimeter experiments that contained activated buffer. The most likely explanation for the observed results is the high rate of particle suspension which results from the restructuring of the buffer during infiltration into a freshly packed lysimeter. This phenomenon seems to override the effect of bed saturation.

SUMMARY AND CONCLUSIONS

Laboratory-scale lysimeter experiments were performed where simulated waste forms were placed in candidate buffer materials chosen for a low-level

radioactive waste repository. Effluent water from the lysimeters and the buffer below the waste form were analyzed for their radionuclide content. The results could not be explained by the traditional solution transport mechanisms, and particle transport was suspected as the dominant mechanism for radionuclide release from the lysimeters. To determine the relative contribution of particle movement to radionuclide transport, several experiments were performed where the waste form was replaced by a layer of buffer containing neutron-activated clay soaked with a solution of water-soluble salts of ^{137}Cs , ^{85}Sr and ^{60}Co prior to placement in the lysimeter. Based on the following evidence, it was concluded that particle transport was responsible for the release of the majority of radionuclides into the effluent water:

(a) The release pattern of clay particles, as traced by neutron-activation products in the effluent water; and the three soluble radionuclides were similar, although a smaller fraction of the soluble isotopes was released.

(b) The concentration profiles of ^{137}Cs , ^{60}Co and the neutron-activation products in the buffer core downstream of the waste form were similar. The differences between the concentration profiles could readily be accounted for by solution transport.

The buffer cores provided the most useful information. The following parameter values were calculated and can be directly used in the modeling of the combined particle-solution transport mechanism:

(1) the filtration coefficient, calculated from the concentration profile of neutron-activation products was 0.3 mm^{-1} ;

(2) the particle adsorption coefficient calculated in a similar manner was 0.08 mm^{-1} ;

(3) the distribution coefficient, computed from the displacement of the soluble radionuclide peaks relative to the neutron-activation product peak was 79 for ^{137}Cs and 8 for ^{85}Sr ;

(4) the desorption rate constant of the soluble radionuclide calculated from the ratio of soluble radionuclide concentration to activation product concentration in the region where particle transport dominates was $2.8 \cdot 10^{-5} \text{ s}^{-1}$ for ^{137}Cs corresponding to a desorption half-life of 6.3 h; and

(5) the adsorption rate constant approximated from the distribution coefficient and the desorption rate constant was found to be $8.3 \cdot 10^{-3} \text{ s}^{-1}$ equivalent to an adsorption half-life of 1.4 min for the same isotope.

When particle transport dominates the release of radio-nuclides through a medium, i.e. before the solution transported radionuclides break through, the relative concentration of radionuclides can be ranked according to their distribution coefficient. Therefore, radionuclides with the highest distribution coefficient should have the highest concentration in the effluent water because they lose the smallest fraction of activity by desorption during transport of particles through the media.

The mechanism of radionuclide transport in lysimeters containing simulated waste forms, such as radionuclide-doped trisodium phosphate in bitumen, was evaluated based in part on the above findings. Experiments with

two candidate buffers were assessed: 90:10 sand-clay mix and 90:10 sand-clinoptilolite mix.

In lysimeters containing the sand-clay mix, the release pattern of ^{137}Cs could be predicted from the combination of waste form leach data and ^{137}Cs release from the lysimeter containing activated clay. Thus the most likely mechanism of release with the effluent water is:

- (1) the release of the dissolved isotope from the waste form;
- (2) adsorption on colloid clay particles, followed by
- (3) particle transport.

The release pattern and concentration profile in the buffer core for ^{60}Co are not consistent with a solution transport mechanism. Similar calculations for ^{60}Co as done for ^{137}Cs predicted a release orders of magnitude lower than actual releases, thus suggesting that the same mechanism postulated for ^{137}Cs does not apply to ^{60}Co transport. The high-pH salts incorporated in the waste form should allow ^{60}Co to be present only as insoluble $^{60}\text{Co}(\text{OH})_2$. Thus, the mobile ^{60}Co is associated most likely with colloids in the waste form, and is released and transported as a component of the colloid particles. The low filtration coefficient suggests small size and/or highly charged negative particles. The assessment of ^{85}Sr transport mechanism is probably the most difficult primarily due to the low solubility of strontium phosphate.

Clinoptilolite contains a few percent bentonite clay that readily washes out of the pore structure. In lysimeters containing a sand-clinoptilolite mixture, the ^{60}Co release is consistent with the mechanism postulated for lysimeters containing sand-clay mix. The ^{85}Sr and ^{137}Cs releases were identical in duplicate lysimeter experiments suggesting the same transport mechanism for both. Based on the shape of the radionuclide concentration profile in the buffer

TABLE 3

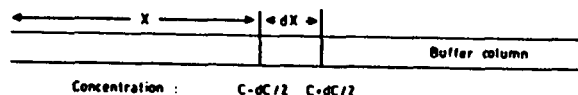
Radionuclide transport mechanisms in lysimeter experiments

Waste form	Buffer	Radionuclide		
		^{60}Co or ^{60}Co	^{137}Cs	^{85}Sr
Activated clay	90:10 sand-clay	clay particle transport + solution transport	clay particle transport + solution transport ($K_d = 79$)	clay particle transport + solution transport ($K_d = 8$)
Trisodium phosphate in bitumen	90:10 sand-clay	cobalt hydroxide particle transport	clay particle transport	?
Trisodium phosphate in bitumen	90:10 sand-clinoptilolite	cobalt hydroxide particle transport	bentonite clay particle transport	bentonite clay particle transport

core, the transport of both radionuclides by polydispersed bentonite particles is postulated. Because clinoptilolite has a very high distribution coefficient for all three of the radionuclides, the significant migration observed could not be attributed to solution transport. In lysimeter experiments, unconsolidated buffers were used. Buffer restructuring during infiltration exaggerates the contribution of particle transport. Radionuclide transport mechanisms are summarized in Table 3 and clearly reflect the importance of particle transport.

APPENDIX — FILTRATION AND COMBINED FILTRATION: RADIONUCLIDE DESORPTION EQUATION

For radionuclides produced by neutron activation, the mechanism of transport is by particle release, particle movement by the action of water and capture by the bed downstream. Particle capture is a first-order process. The filtration coefficient, w , is applicable to mono-dispersed particles and is defined as the fraction of particles removed per unit bed depth. Consider a buffer column with a cross-sectional area A , and with particulate laden water percolating through it at a pore-water velocity of $V \text{ cm s}^{-1}$. Compute a mass balance for a radionuclide that is a neutron-activation product for a section $X \text{ cm}$ downstream with thickness $dX \text{ cm}$.



(input) - (output) = (accumulation)

$$(C - dC/2)VA - (C + dC/2)VA = CVAwdX$$

$$dC = -CwdX \quad \text{and} \quad dC/ = -wdX$$

upon integration:

$$\ln C/C_0 = -wX \quad (\text{A-1})$$

where C = concentration of radionuclide (neutron-activation product).

For adsorbed radionuclides in addition to the filtration process described above, the radionuclide desorption process is also responsible for radionuclide transfer from the solution to the packed bed. Applying the mass-balance equation for an adsorbed radionuclide and assuming first-order kinetics for the desorption process:

$$(C^* - dC^*/2)VA - (C^* + dC^*/2)VA = C^*VAwdX + C^*VAGdX \quad (\text{A-2})$$

where G = first-order rate constant for radionuclide desorption; dt = residence time for particle in buffer core $dX \text{ cm}$ long; and C^* = concentration of adsorbed radionuclide.

Assuming that the particles travel at the same velocity as the pore water:

$$Vdt = dX \quad (\text{A-3})$$

Combining eqs. A-2 and A-3, we get:

$$dC^*/C^* = -wdX - (G/V)dX$$

and upon integration:

$$\ln (C^*/C_0^*) = wX - (G/V)X \quad (\text{A-4})$$

Substituting eq. A-1 into eq. A-4 we get:

$$\ln (C^*/C) = \ln (C_0^*/C_0) - (G/V)X$$

REFERENCES

- Buckley, L.P., Tosello, N.B. and Woods, B.L., 1987. Leaching low level radioactive waste in simulated disposal conditions. In: P.L. Cote and T.M. Gilliam (Editors), *Environmental Aspects of Stabilization and Solidification of Hazardous and Radioactive Wastes*. Am. Soc. Test. Mater., Philadelphia, PA, ASTM STP 1033, pp. 330-342.
- Buckley, L.P., Philipose, K.E. and Torok, J., 1988. Engineered barriers and their influence on source behaviour. Presented at Int. Symp. on Management of Low- and Intermediate-Level Radioactive Wastes, Stockholm, May 16-20, 1988. Sponsored by Int. At. Energy Agency, Vienna, in cooperation with Comm. Eur. Commun., Brussels (Ref. Pap. IAEA-SM-303-120).
- Champlin, J.B.F. and Eichholz, G.G., 1976. Fixation and re-mobilization of trace contaminants in simulated subsurface aquifers. *Health Phys.*, 30: 215-219.
- Eichholz, G.G., Wahlig, B.G., Powell, G.F. and Craft, T.F., 1982. Subsurface migration of radioactive waste materials by particulate transport. *Nucl. Technol.*, 58: 511-520.
- Gimblett, F.G.R., 1963. *Inorganic Polymer Chemistry*. Butterworths, London, 77 pp.
- Nilsson, K., Jensen, B.S. and Carlsen, L., 1985. The migration chemistry of cobalt. *Eur. Appl. Res. Rep.-Nucl. Sci. Technol.*, 7(1): 23-86.
- Ohtsuka, Y., Takebe, S., Yamamoto, T. and Wadachi, Y., 1988. Migration behaviour of radionuclides (^{60}Co , ^{85}Sr and ^{137}Cs) in an aquifer. *J. Nucl. Sci. Technol.*, 25(2): 165-168.
- Parks, G.A., 1965. The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems. *Chem. Rev.*, 65: 177-198.
- Saltelli, A., Avogadro, A. and Bidoglio, G., 1984. Americium filtration in glauconitic sand columns. *Nucl. Technol.*, 67: 245-254.
- Sheppard, J.C., Campbell, M.J., Cheng, T. and Kitrick, J.A., 1980. Retention of radionuclides by mobile humic compounds and soil particles. *Environ. Sci. Technol.*, 14: 1349-1353.
- Torok, J. and Buckley, L.P., 1988. Physical and chemical environment and radionuclide migration in a low-level radioactive waste repository. *At. Energy Can., Ltd., Rep. AECL-9685*.
- Travis, B.J. and Nuttal, H.E., 1985. Analysis of colloid transport. In: M.O. Werme (Editor), *Scientific Basis for Nuclear Waste Management, IX*. Mater. Res. Soc. Publ., 50: 737-745.